

REPLY TO PLANAVSKY ET AL.:

# Strong evidence for high atmospheric oxygen levels 1,400 million years ago

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Planavsky et al. (1) argue that variability in the V/Al of soils compromises our ability to detect V depletions and thus oxygenated bottom waters in the Xiamaling Formation. Indeed, because of such variability, we explored trace metal chemistry through several units of the Xiamaling Formation to establish V/Al background values and trace metal behavior. Unit 4 lacks trace metal enrichments, with V/Al values distributed around the crustal average (CA) (Fig. 1A), which we take to represent unaltered particles entering the basin. In contrast, unit 3 was enriched in Mo and U, with V/Al either depleted or similar to CA (Fig. 1A). These trace metal patterns are, in the modern ocean, uniquely found in organic-rich sediments depositing in oxygenated water (2). In contrast, unit 2 was enriched in V, Mo, and U, a pattern found under anoxic depositional conditions (2). If, following ref. 1, unit 3 bottom waters were similarly anoxic, then deposition somehow switched to a source so low in V/Al that the sediment V/Al remained  $\leq$  CA despite enriching in V as expected under anoxic deposition. There is no modern precedent for such trace metal behavior under anoxic deposition (2), and we view this scenario as unlikely. We believe that unit 3 bottom water oxygenation is the most parsimonious with basin particle chemistry and modern analogs.

Planavsky et al. (1) argue that our 2,3,6-trimethyl aryl isoprenoid (TMAI) biomarkers are a product of contamination. They cite previous work (3) finding no evidence of these biomarkers in six black shale outcrop samples. We share concerns about contamination and sample integrity, and therefore analyzed fresh core material collected with fresh water as a

drilling fluid. We have compared many results from core and outcrop material (collected from fresh road cuts), often noting very different biomarker patterns and even the absence of 2,3,6-TMAIs in outcrop samples where stratigraphically equivalent core material contains them. Thus, we believe that our 2,3,6-TMAI detection is robust. Both our geochemical data and modeling of minimum oxygen levels reconstruct an ancient oxygen minimum zone (OMZ) setting. We emphasize, however, that our minimum oxygen estimates do not require evidence of an ancient OMZ; our oxygen estimates are based solely on reproducing bottom water oxygenation. If there were no OMZ, however, our model would generate considerably higher estimates of atmospheric oxygen.

Planavsky et al. (1) challenge that chromium isotope systematics suggest much lower concentrations of Mesoproterozoic atmospheric oxygen (4). This interpretation rests on an authigenic seawater source for the Cr. Laser ablation inductively coupled plasma mass spectrometry analyses of the Mesoproterozoic and late Paleoproterozoic samples used for Cr isotope analysis produced linear trends in Ti vs. Cr concentration as expected for detrital material (Fig. 1B). Furthermore, ratios of Cr/Ti above the CA could have easily resulted from variability in the trace metal content of depositing sediment, as highlighted by ref. 1. Therefore, there is little evidence that these samples contain authigenic Cr, which is essential for oxygen reconstructions.

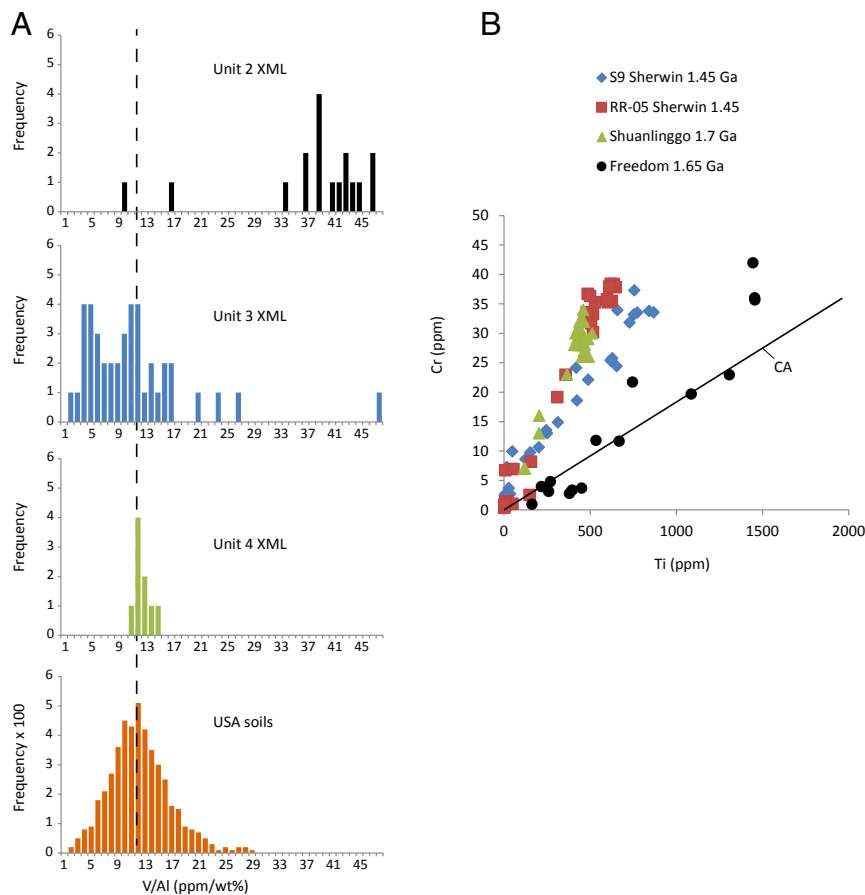
Thus, we believe that our result of elevated Mesoproterozoic oxygen concentration is most parsimonious with the available geochemical evidence.

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**Fig. 1. (A)** Frequency diagram of V/Al ratio for top soils from the United States (*Bottom*) and for the various units from the Xiamaling Formation: units 2 (*Top*), 3 (*Upper Middle*), and 4 (*Lower Middle*). Soil plot (*Bottom*) is reproduced from ref. 1, and Xiamaling data are from ref. 2. The dotted line represents the crustal average (CA) V/Al (5). (**B**) Laser ablation results for Cr and Ti for Mesoproterozoic and late Paleoproterozoic samples (data from ref. 4). The CA (5) slope is given by the black line.

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